

Supporting Information

Pt-NPs/MWNT Nanohybrid as a Robust and Low-cost Counter Electrode Material for Dye-sensitized Solar Cells

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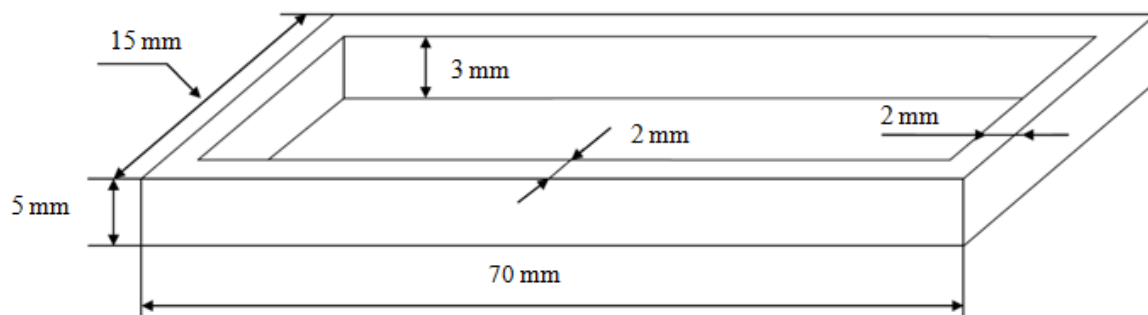
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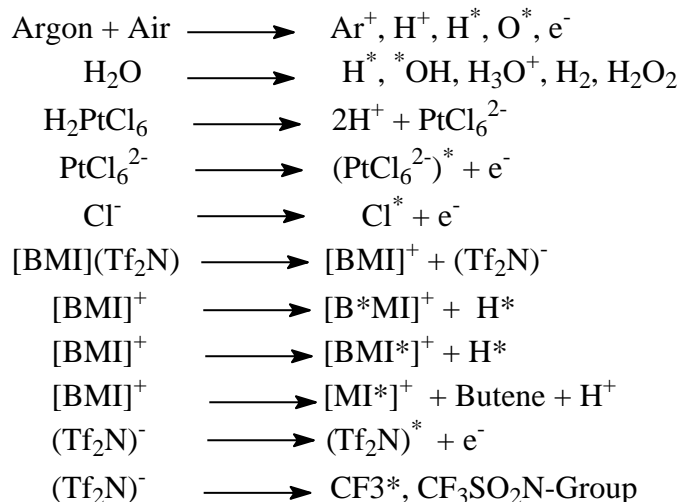
Purification of MWNTs

The purified MWNTs (Hanwha Nano Tech, Korea) were obtained after thermal treatment for 60 min at 300 °C in air. After mixing with hydrochloric acid (37%), sonication for 1 hour and filtration at least 5 times were performed until the pH of the solution was neutral. After drying them in an oven at 60 °C for 24 hours [S1], all of the amorphous carbonaceous, graphitic nanoparticles, carbon nanoparticles and catalyst impurities were removed.



Scheme 1: Scheme of a reactor

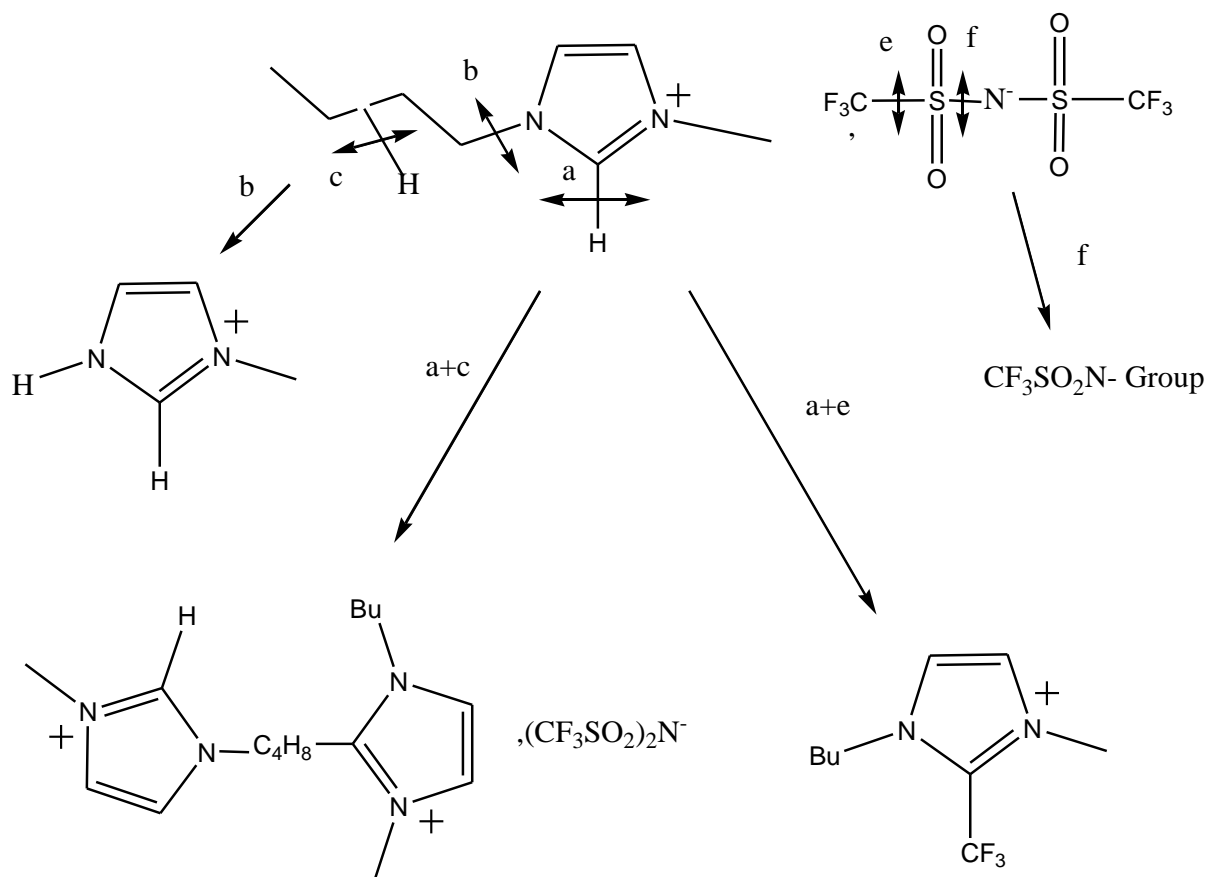
Formation of reducing agents



Scheme S2. Formation scheme of reducing agents through plasma treatment [S2].

Hydrogen radicals and electrons are the main reducing agents for the formation of the Pt-NPs through the atomization reaction of the Pt precursors at the interface between the plasmas and RTIL. They are generated by the atmospheric pressure plasma in contact with water and oxygen from the atmosphere during the plasma treatment, as described in the equation of Scheme S2. In the RTIL solution containing MWNTs and Pt precursor salt, they can also be generated from the impurity water in the RTIL or water adsorbed on the precursor salt. Besides, e^- may be formed by photodetachment from anions such as chloride ions, which are known to form C-H...Cl interactions with the 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide ([BMI](Tf₂N)) cations, under the plasma irradiation of argon.

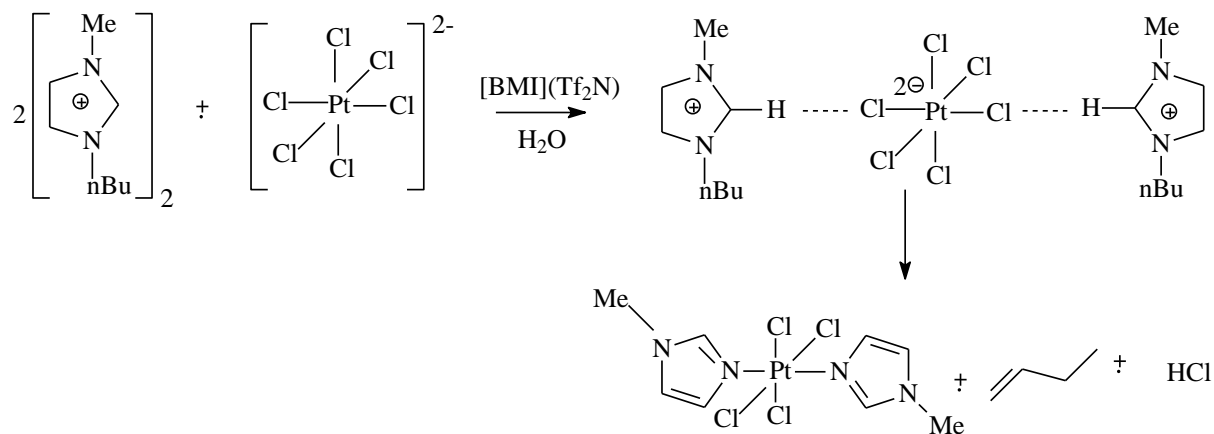
Formation of Ionic Liquid Supramolecule (ILSM)



Scheme S3. Simplified degradation scheme of [BMI][Tf₂N] [S3].

The ILSM can be simultaneously formed through the recombination of radicals dissociated from the RTIL monomer under the high energy plasma flame. The primary [BMI*]⁺ cation radicals can be formed after the homolytical dissociation of the C-H bonds in the imidazolium ring (**process a in Scheme S3**). [MI*]⁺ cation radicals can be formed after the loss of the butyl group (**process b in Scheme S3**). [B*MI]⁺ cation radicals can be formed after the loss of a hydrogen atom from the butyl chain (**process c in Scheme S3**). CF₃^{*} and TfN^{*} radicals can be formed from the [Tf₂N]⁻ anion (**processes e and f in Scheme S3**). The recombination of these radicals can produce ILSMs (**process a+c and a+e in Scheme S3**).

Formation of Pt complex



Scheme S4. Reaction of the imidazolium cation under neutral conditions [S4].

Due to the interaction between the chloride ions and hydrogen of RTIL, the complex, [BMI]₂PtCl₄, can be formed from the Pt compound and [BMI]Tf₂N at around 65°C.

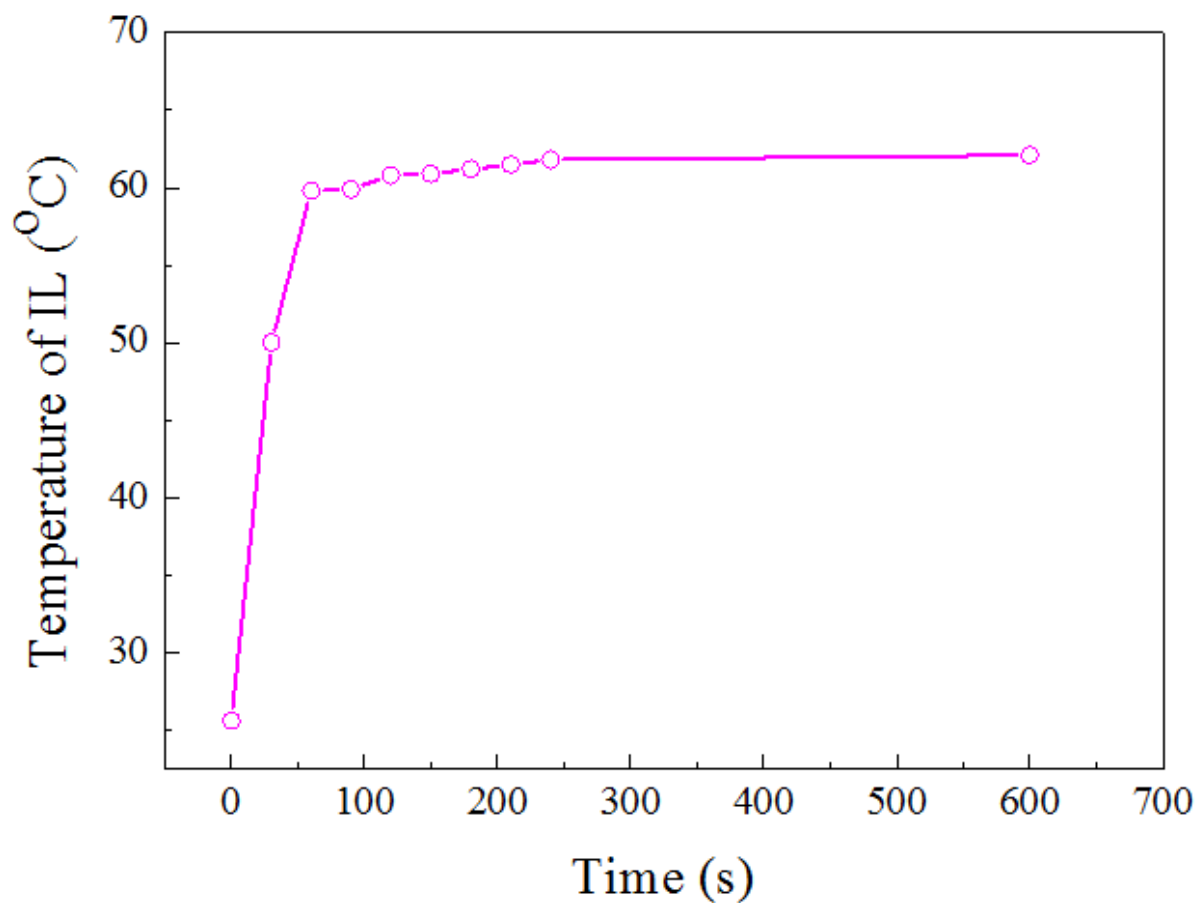


Figure S1. Change of ionic liquid solution temperature during plasma treatment.

The change of the temperature of the ionic liquid solution during the plasma treatment was measured with a thermocouple installed in a temperature controlling device (Testo 175). The temperature increased to above 60°C within 100 sec and then leveled off at around 65°C.

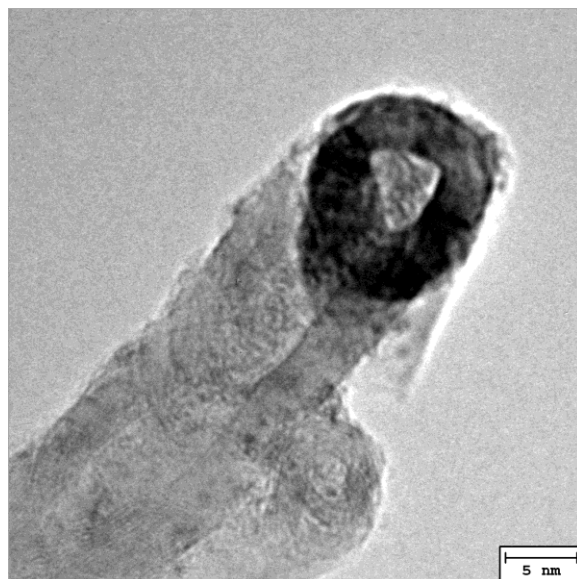


Figure S2. TEM image of the multi-wall carbon nanotubes (MWNTs) with their ends open.

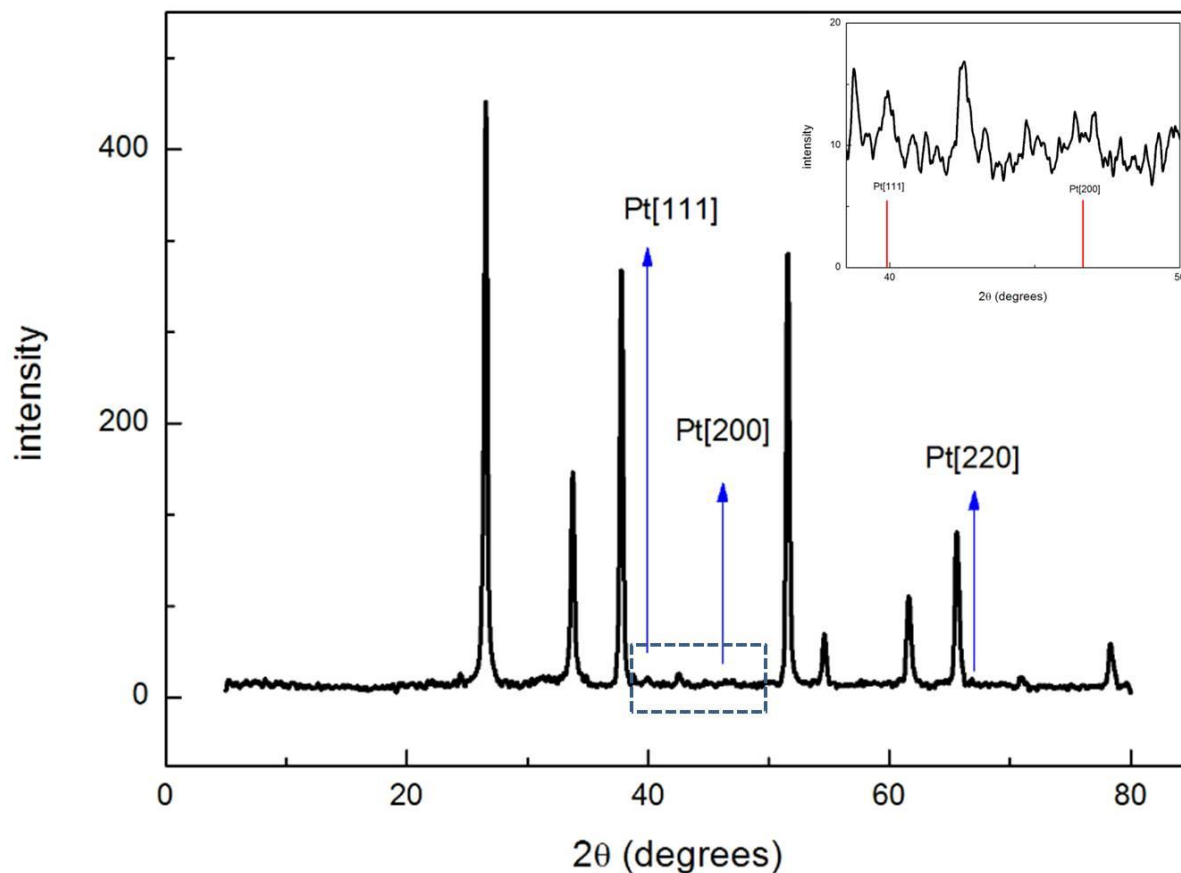


Figure S3. XRD pattern of MWNT/Pt nanohybrids.

Figure S3 shows the XRD patterns of the MWNT/Pt nanohybrid samples on the FTO-glass substrate. The single broad diffraction peak at around $2\theta = 26.46^\circ$ belongs to the MWNT support. All of the XRD patterns of the MWNT/Pt nanohybrid sample exhibit the characteristic diffraction peaks of Pt (111) at $2\theta = 39.7^\circ$, Pt (200) at $2\theta = 46.2^\circ$ and Pt (220) at $2\theta = 67.4^\circ$, indicating that Pt is present in the face centered cubic (FCC) phase. The inset in Figure S5 shows the detailed scan of the Pt (111) and Pt (200) peaks.

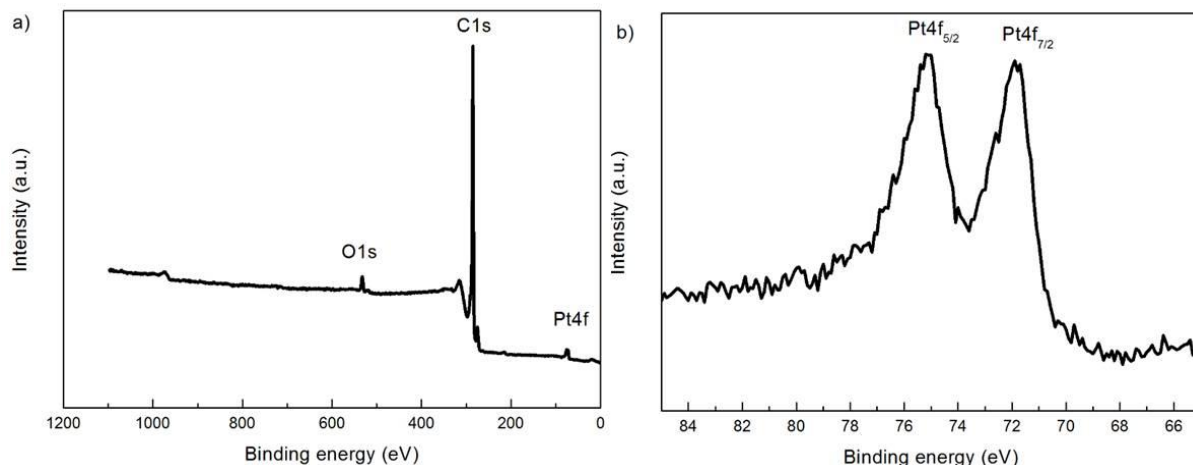


Figure S4. (a) XPS survey spectra and (b) Pt4f spectra of MWNT/Pt nanohybrids.

The electronic state of Pt in the MWNT/Pt nanohybrid is measured by XPS. Figure S4 shows the XPS survey spectra and Pt4f XPS spectra of the MWNT/Pt hybrid. The Pt, C and O signals, obtained from the XPS survey spectra in Figure S4 (a), must come from the Pt precursor, MWNTs and purification process, respectively. Figure S4 (b) displays the Pt4f core level spectra of the MWNT/Pt nanohybrid sample. The intensive doublet at 71.85 eV and 75.25 eV indicates the presence of metallic Pt [S5].

References

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